Surface Modification of Ordered Nanoporous Carbons CMK-3 via a Chemical Oxidation Approach and its Application in Removal of Lead Pollution from Water

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Abstract—Lead has been well recognized for its negative effect on the environment where it accumulates readily in living systems. The aim of this study is surface modification of ordered nanoporous carbons CMK-3 using nitric acid as oxidizing agent. Furthermore, the modified nanoporous carbon, OCMK-3, was used as a nanoadsorbent for removal of Pb(II) from water. In this work, ordered mesoporous carbons were synthesized using SBA-15 silica as template. The structural order and textural properties of the mesoporous materials were studied by XRD, FT-IR, nitrogen adsorption-desorption, SEM and TEM. In order to study the effect of various operating parameters such as initial concentration, contact time and adsorbent dose on the adsorption capacity of Pb(II), batch sorption experiments were conducted. The results indicate that the time required for equilibrium is 2 h and order of adsorption in terms of the removal percentage is: OCMK > CMK-3. Boehm titration showed that the oxidation with nitric acid can selectively increase the carboxylic groups on the CMK-3. Moreover, the FT-IR spectra demonstrated a significant increase in the C-O and –COOH functional groups. Thus it can be said that the carboxylic functional groups are mostly responsible for binding heavy metal ions for OCMK-3. Our results show that the modified mesoporous carbon is an effective nanoadsorbent for lead pollution remediation in the environment.

Keywords- Nanoporous Carbons; Modification; Lead; Pollution

I. INTRODUCTION

Lead (Pb) is attracting wide attention of environmentalists as one of the most toxic heavy metals. The sources of lead release into the environment by waste streams are battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, painting, dying, and other industries [1-2]. Lead has been well recognized for its negative effect on the environment where it accumulates readily in living systems. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths [3]. Out of the wastewater treatment methods involving lead, precipitation, coagulation-sedimentation, reverse osmosis, ion exchange, cementation, and adsorption onto activated carbon, adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions, economics, and handling [4-5]. Various adsorbents such as activated carbon, iron oxides, filamentous fungal biomass and natural condensed tannin have been explored [6]. EPA drinking water standards for lead are 0.05 mg/l, but a level of 0.02 mg/l has been proposed and is under review [4]. Increasingly stringent standard on the quality of drinking water has stimulated a growing effort on the exploitation of new high efficient adsorbents. Recent works have shown that mesoporous materials can have large adsorption capacity, good selectivity and improved powder recoverability for the removal of toxic compounds from aqueous solutions [7-8]. Mesoporous materials are a class of nanoporous materials that were discovered at 1992 by the Mobil oil researchers [9]. Mesoporous carbon materials with ordered pore structure, high pore volume, high specific surface area, and tunable pore diameters can be used as an effective adsorbent in industry. Ordered mesoporous carbons (OMCs) templated by ordered mesoporous silicas (OMSs) have been extensively studied; especially CMK-3 carbons [10] templated by SBA-15 silicas, respectively. Due to the nature of this templating synthesis involving introduction of carbon precursor into pores of the template followed by carbonization and template dissolution, inverse carbon replicas of the OMS templates are obtained. Modification of the surface chemistry of mesoporous carbons might be a viable attractive route toward novel applications of these materials. A modified mesoporous carbon containing different functional groups such as carboxyl, hydroxyl and amine could be used for technological applications such as extracting metallic cations from aqueous and nonaqueous solutions, in catalysis, for treatment of waste and toxic effluents produced by a variety of chemical processes, etc. Acid treatment was generally used to oxidize the porous carbon surface; it enhanced the acidic property, removed the mineral elements and improved the hydrophilic of surface [11]. The objective of this study is to modify the surface chemistry of ordered mesoporous carbons, creating functional groups, whereas their ordered structure is maintained. In this work, ordered mesoporous carbons were synthesized using SBA-15 silica as template.
Their texture and surface chemistry were modified by oxidation treatments in liquid phase using nitric acid as oxidizing agent. Furthermore, this modified nanoporous carbon was used as a nanoadsorbent for removal of Pb(II) from water.

II. MATERIALS AND METHODS

A. Synthesis of SBA-15

The reactants used for synthesis of SBA-15 were tetraethyl orthosilicate (TEOS, 98%) as a silica source, deionized water, Pluronic® P123 (EO30PO70EO30) as a surfactant and phosphoric acid (H3PO4, 85%) from Aldrich (U.K.). Mesoporous silica SBA-15 was synthesized as reported by Colilla et al. [12]. The synthesis procedure was based on the use of Pluronic® P123 (EO30PO70EO30) as directing agent of the silica mesostructure and phosphoric acid as catalyst. The template agent was dissolved in H3PO4. The molar compositions of the solutions here presented are as follows: SiO2/P123/H3PO4/H2O=1/0.017/1.5/208. TEOS was used as silica precursor. These solutions were stirred at 35 ºC for 24 h in sealed Teflon beakers and then further heated at 100 ºC for 24 h. The obtained products were filtered, washed with deionized water and then dried at 90 ºC for 12 h in air. The surfactant removal consisted in a two-steps procedure based on heating first at 250 ºC for 3 h, and then at 550 ºC for 4 h in air.

B. Synthesis of CMK-3

The reactants used for synthesis of CMK-3 were sucrose as a carbon source, sodium hydroxide (NaOH), ethanol, and sulfuric acid (H2SO4, 98%) as a catalyst for synthesis of ordered mesoporous carbon CMK-3 from Merck, Germany. CMK-3 was prepared according to the synthesis procedure described by Ryoo et al. [13]. SBA-15 was used as a hard template. In a typical synthesis, 1 g SBA-15 was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H2SO4 in 5 g H2O. The resulting mixture was dried in an oven at 100 ºC (6 h) and subsequently the oven temperature was increased to 160 ºC. After 6 h at 160 ºC, the SBA-15 silica containing the partially carbonizing organic masses was added in aqueous solution consisting 0.75 g of sucrose, 0.08 g of H2SO4 and 5 g of water. The resultant mixture was dried again at 100 ºC (6 h), and subsequently, the oven temperature was increased to 160 ºC (6 h). The color of the sample turned very dark brown or nearly black. This powder sample was heated to 900 ºC under vacuum using a fused quartz reactor. The carbon-silica composite thus obtained was washed with 1 M NaOH solution of 50% ethanol-50% H2O twice at 90 ºC in order to dissolve the silica template completely. The carbon samples obtained after the silica removal were filtered, washed with ethanol and dried at 120 ºC.

C. Modification of CMK-3

The texture and surface chemistry of synthesized CMK-3 was modified by means of oxidation treatment in liquid phase. CMK-3 was oxidized by nitric acid under optimal oxidation condition, such as nitric acid concentration and oxidation temperature [11]. 0.1 g of dried CMK-3 powder was treated with 15 ml of HNO3 solution (2 M solution) for 1 h in the 80 ºC under refluxing. After oxidation, samples were recovered and washed thoroughly with distilled water until the pH was close to 7. Finally, carbon supports were filtered, washed with distilled water and dried at 108 ºC for 12 h. It was denoted by OCMK-3.

D. Determination of Surface functional groups

Surface functional groups of the adsorbents were determined by the method of Boehm [14]. On the Boehm titration the following assumptions were made to distinguish the surface carbon-oxygen complexes according to their acidity: NaOC2H4 neutralizes carboxylic, lactonic, phenolic, and carbonyl groups; NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na2CO3 neutralizes carboxylic and lactonic groups; NaHCO3 only neutralizes carboxylic groups. One gram of the adsorbent was separately mixed with 15 mL of the above-mentioned basic solutions, and agitated at 100 rpm for 4 days to complete the neutralization. Five millilitre of remaining basic solution was separated from the adsorbent, and back titration was carried out by 0.1 M hydrochloric acid using methyl red as a color change pH indicator (Table 1).

E. Adsorption studies

In order to study the effect of various operating parameters such as initial concentration, contact time and adsorbent dose on the adsorption capacity of Pb(II), batch sorption experiments were conducted. Stock solutions of 1000 mg/l Pb(II) were prepared from Pb(NO3)2 as the lead source in deionized water containing a few drops of concentrated HNO3 to prevent hydrolysis formation.

A series of aqueous solutions of lead with the initial concentrations of 10, 50, 100, 200 and 400 mg/l and doses of 0.1, 0.3, 0.5 and 0.7 g/l were prepared. The resulting mixtures were continuously shaken in a shaking bath with agitation times of 10, 20, 30, 60, 120, 240 and 360 min at the speed of 150 rpm. The adsorbent was separated with Whatman-filter paper and the concentration of lead in the supernatant was analyzed with an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES-Perkin-Elmer 4300 DV Model). The adsorption capacities based on the differences of the concentrations of solutes before and after the experiment were calculated by

\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

(1)

where \( q_e \) is the adsorption capacity (mg/g) of the adsorbent at equilibrium; \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of solute (mg/l), respectively; \( V \) is the volume of the aqueous solution (l) and \( W \) the mass (g) of adsorbent used in the experiments. The percentages of lead removal (\( R \)) were calculated by

\[ R(\%) = \frac{(C_0-C_e)}{C_0} \times 100 \]  

(2)

<table>
<thead>
<tr>
<th>Surface functional groups, meq/g</th>
<th>CMK-3</th>
<th>OCMK-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic groups</td>
<td>0.14</td>
<td>1.30</td>
</tr>
<tr>
<td>Lactonic groups</td>
<td>0.16</td>
<td>0.16</td>
</tr>
</tbody>
</table>
where $C_i$ and $C_e$ are the initial and equilibrium concentrations of pollutant (mg/l), respectively.

**F. Physical and structural characterization**

The X-ray powder diffraction (XRD) patterns were recorded on a Philips 1830 diffractometer using Cu Kα radiation. The Fourier transform infrared spectra (FT-IR) spectra for the samples were measured on a DIGILAB FTS 7000 instrument. Textural properties of the synthesized samples were characterized by N₂-physisorption. Adsorption-desorption isotherms of the synthesized samples were measured at 77 K on micromeritics model ASAP 2010 sorptometer. Pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method, while surface area of the sample was measured by Brunauer-Emmet-Teller (BET) method. Scanning electron microscopy (SEM) images were obtained with JEOL 6300F SEM and Transmission electron microscopy (TEM) images were obtained using a 300 kV Philips CM-30 TEM.

**III. RESULTS AND DISCUSSION**

A. Characterization

The X-ray diffraction of ordered mesoporous material, CMK-3 and OCMK-3 are shown in Fig. 1. The XRD patterns of CMK-3 showed three diffraction peaks that can be indexed to (100), (110) and (200) in the $2\theta$ range from 0.5-10°, representing well-ordered hexagonal pores. The XRD patterns show well-resolved reflections indicating that CMK-3 nicely maintains its original structure even after the modification with HNO$_3$. The XRD patterns indicate that both samples have highly ordered uniform mesopores. Fig. 2 shows the FT-IR spectra of CMK-3 and OCMK-3. Bands at 1000-1300 cm$^{-1}$ denote the absorption of stretching vibration of C–O bonds. The other peak at 1713 cm$^{-1}$ can be assigned to the stretching and bending vibration modes of –COOH on the surface of carbon materials. Furthermore, another band at around 3533 cm$^{-1}$ was observed in CMK-3.

**Figure 1.** XRD patterns of CMK-3 and OCMK-3.

It was mainly caused by the O–H stretching vibration of the adsorbed water molecules. The intensity of 3533 cm$^{-1}$ band in OCMK-3 was similar to CMK-3. The relative intensity of 1103, 1192 and 1713 cm$^{-1}$ bands in OCMK-3 were higher than those of the CMK-3 sample, indicating that more C–O and –COOH functional groups were introduced when the oxidation was done. Thus, the efficiency of the modification with nitric acid is demonstrated by a significant increase in the C–O and –COOH functional groups (Fig. 2).

From the nitrogen sorption isotherms (Fig. 3) of mesoporous carbon type carbons, it can be seen that after modification with HNO$_3$, the obtained carbons still have type IV isotherms, indicating that mesoporosity is still preserved and all of them are mesoporous materials. Fig. 3 shows the N$_2$ sorption isotherms of CMK-3 and OCMK-3. The BET surface areas and pore volumes of CMK-3 and OCMK-3 were calculated (Table 2). The lower surface areas and pore volumes of OCMK-3 compared with CMK-3 are mainly attributed to the presence of dense carboxylic surface groups. Calculating pore diameters of mesoporous materials using the BJH method is common.

**Figure 2.** FT-IR spectra of CMK-3 and OCMK-3 samples.

**Figure 3.** Adsorption-desorption isotherms of nitrogen at 77 K on CMK-3 and OCMK-3.
The narrow pore size distributions, centered at about 4.3 nm for CMK-3 and 3.9 nm for OCMK-3, clearly demonstrate that the modification did not alter the mesopore structure of CMK-3.

Scanning electron microscopy images of SBA-15 and CMK-3 samples are shown in Fig. 4A-B. SEM images reveal that the synthesized SBA-15 sample (Fig. 4A) consists of many rope-like domains, aggregated into wheat-like macrostructures. The SEM image for the carbon synthesized is shown in Fig. 2B. The carbon replica possesses the same wheat-like shape similar to the SBA-15 template. Transmission electron microscopy (TEM) images of synthesized samples are shown in Fig. 4C-D. TEM image showed in Fig. 4C confirm that the structure of CMK3 is well-ordered hexagonal arrays of mesopores. Fig. 5D shows that after oxidation treatments, ordered structure is maintained.

### Table 2. Textural parameters of the CMK-3 and OCMK-3.

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>Pore size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-3</td>
<td>4.3</td>
<td>998</td>
<td>1.40</td>
</tr>
<tr>
<td>OCMK-3</td>
<td>3.9</td>
<td>985</td>
<td>1.25</td>
</tr>
</tbody>
</table>

**B. Adsorption studies**

Fig. 5 shows percentage of lead removal on the OCMK-3 at various initial concentrations and agitation times. It is seen that the adsorption of Pb(II) on OCMK-3 decreased from 65 to 29 % by increasing Pb(II) concentration from 10 to 400 mg/l at 360 min. Sufficient adsorption sites are available at lower concentration, but at higher concentration metal ions are greater than sites. The distribution of adsorbate between adsorbent and solution is influenced by agitation time. In general, a two-stage kinetic behavior was observed (Fig. 5): rapid initial adsorption in a contact time of 1 h, followed by a second stage with a much lower adsorption rate. This is obvious from the fact that a large number of vacant surface sites are available for the adsorption during the initial stage and with the passage of time. Therefore, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase. Fig. 5 also indicates that the time required for equilibrium is 2 h. In general, carbon mesoporous is not nearly effective at removing inorganic pollutants as it is in removing organic compounds. Therefore, the adsorption capacities and the feasible removal rates must be substantially boosted by modification of the carbon with suitable chemicals. For this reason, modification technique was used to increase surface adsorption. In order to evaluate the efficiency of the modification, the adsorption of the lead on CMK-3 was measured. Fig. 5 shows that the maximum removal of Pb is 65 % for initial concentration of 10 mg/l for OCMK-3 after 360 min. This value is 40 % for CMK-3 (Fig. 6). Thus, from these figures it is seen that the order of adsorption in terms of the removal percentage is: OCMK > CMK-3. The effect of adsorbent dose on adsorption amount $q_e$ (mg/g) of lead was illustrated in Fig. 7. The amount of adsorption for lead was increased with adsorbent dose. This increase in loading capacity is due to the availability of greater amounts of active sites of the adsorbent [15]. The results of Boehm titration show that the oxidation with nitric acid can selectively increase the carboxylic groups on the CMK-3 as shown in Table 1. Furthermore, the FT-IR spectra show a significant increase in the C–O and –COOH functional groups (Fig. 2). Thus it can be said that the carboxylic functional groups are mostly responsible for binding heavy metal ions for OCMK-3.

![Figure 4. Images of samples. (A) SBA-15: SEM, (B) CMK-3: SEM, (C) hexagonal structure of CMK-3: TEM, (D) oxidized mesoporous carbon (OCMK-3): TEM.](image)

![Figure 5. Effect of initial concentration and agitation time on removal of lead by OCMK-3 (adsorbent dose: 0.5 g/l, pH: 6 and temperature: 25 °C).](image)

At this study using adsorption isotherms, the aximum adsorption capacity, was found to be 333 mg/g for OCMK-3.
and 250 mg/g for CMK-3. Wang et al. [16] prepared Mn oxide-coated carbon nanotubes (MnO2/CNTs) and used it for removal of Pb(II) from aqueous solution. The maximum adsorption capacity was 78 mg/g. Also at another study, the maximum adsorption capacity of Pb(II) on sea nodule residues was 107 mg/g [4]. We conclude that the adsorption of the Pb(II) from the solutions onto the ordered nanoporous carbons CMK-3 will be improved by surface modification of CMK-3 via a chemical oxidation approach. The results obtained confirm that CMK-3 and OCMK-3 were successfully prepared. The presence of lead in wastewater and surface water is becoming a severe environmental and public health problem. Our results show that the modified mesoporous carbon, OCMK-3, is an effective nanoadsorbent for lead pollution remediation in the environment.

ACKNOWLEDGMENT

We sincerely thank Iran Nanotechnology Initiative Council. We also appreciate National Elite Foundation of Iran for their support.

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[11] P.A. Bazula, A.H. Lu, J.J. Nitz, and F. Schuth, “Surface and pore structure modification of ordered mesoporous carbons via a chemical oxidation approach. The results obtained confirm that CMK-3 and OCMK-3 were successfully prepared. The presence of lead in wastewater and surface water is becoming a severe environmental and public health problem. Our results show that the modified mesoporous carbon, OCMK-3, is an effective nanoadsorbent for lead pollution remediation in the environment.

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